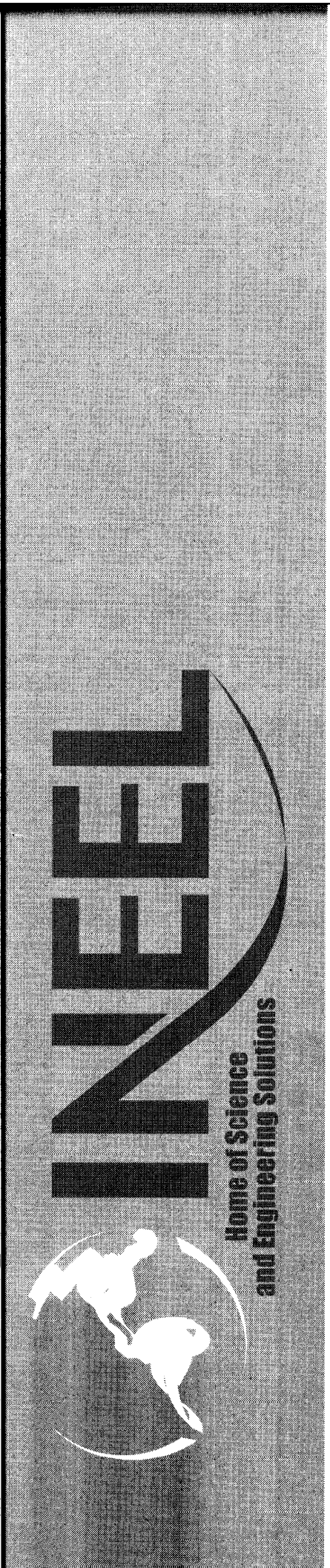

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FINAL REPORT

COLUMN TESTS TO STUDY THE TRANSPORT OF PLUTONIUM AND OTHER RADIONUCLIDES IN SEDIMENTARY INTERBED AT INEEL

submitted by

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to

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December 21, 2000

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SUMMARY

The purpose of this report is to document the results of laboratory studies, primarily column experiments, on the mobilities of selected radionuclides in sedimentary interbed from the Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL). The work was motivated by routine environmental monitoring data which are inconsistent with predictions based on classical advection/dispersion/sorption theory in which contaminant mobility is inferred from distribution coefficients measured in batch partitioning experiments. Whereas plutonium and americium mobilities estimated through this approach are extremely low and interbed is predicted to be an effective barrier to migration, the field data suggest they may have penetrated one or more interbed layers.

There are both hydrological and chemical/geochemical mechanisms, acting either separately or in combination, that can explain these observations. This project focused on chemical/geochemical mechanisms that may affect the mobilities of various actinides, especially plutonium, in sedimentary interbed. The initial objective was to determine if high mobility forms of plutonium were possible in laboratory columns eluted with a perched water simulant. As the project progressed, the scope expanded to include uranium and americium, which are important contaminants at the SDA, as well as thorium and neptunium, which are often used as analogs for plutonium(IV) and plutonium(V), respectively. The objectives were also extended to include mechanistic explanations for the observed behaviors, which is critical for determining if the phenomena observed in the laboratory setting are relevant in the field.

Column experiments were performed using unconsolidated interbed collected from nearby cores and various ground water simulants containing elevated concentrations of potential complexing agents. The interbed sample was composited from five cores taken from different depths. Most of the experiments were conducted with the less than 250 μm size fraction, although the 106-250 μm size fraction was used in selected experiments. The ionic species in the ground water simulants were based on analyses of perched water from the site. The perched water simulant (PWS) also contained humic acid and ethylenediaminetetraacetic acid (EDTA), based on their extensive presence in natural waters and low level radioactive wastes, respectively. The modified perched wa-

ter simulant (MPWS) had the same ionic composition as the PWS, but it did not contain either humic acid or EDTA.

The experimental apparatus consisted of reservoirs for the perched water simulant and the spiked simulant, a peristaltic pump, the column packed with sedimentary interbed, and a fraction collector. The spiked simulant was introduced into the column as a finite step of approximately one pore volume in width. Following the spike, the column was eluted with anywhere from 10 to more than 1000 pore volumes of unspiked simulant. Analyses of the effluent fractions were performed with an alpha/beta discriminating liquid scintillation counter. This made it possible, in a single test, to simultaneously measure a beta emitter, such as stronium-85, and an alpha emitting actinide. The data are displayed graphically in the form of breakthrough curves, *i.e.* normalized effluent concentration (effluent concentration divided by concentration in spike) versus time (expressed as displaced pore volumes, DPV, which is the integrated volumetric flow divided by the pore volume). The breakthrough curves are quantitatively characterized by the retardation factor and the corresponding fractional recovery.

The breakthrough curves for strontium were characterized by a single peak containing, within the limits of experimental uncertainty, all of the radioactivity in the spike. The retardation factor was consistently between 200 and 300 for both the PWS and the MPWS. Uranium breakthrough was also characterized by a single peak containing all of the radioactivity in the spike. However, uranium was much more mobile than strontium, with retardation factors between 3 and 4. The breakthrough curves for the other actinides differed significantly from those for uranium. Under the influence of the PWS, the curves for americium, thorium, plutonium(IV), neptunium, and plutonium(V) were all characterized by multiple components having distinctly different mobilities. There was a small, (<<1%) high mobility component that emerged within the first few DPV; a large (≈50%), intermediate mobility component that emerged between a few DPV and 500 DPV (not present for plutonium(V)); and a large, low mobility component that was retained in the column. For the MPWS (*i.e.* in the absence of EDTA and HA), in excess of 99% of the americium, thorium, plutonium(IV), and plutonium(V) had very low mobility (R>1000).

Based on the results of the column experiments, batch filtration studies, and thermodynamic calculations, three major conclusions are drawn regarding actinide transport under the influence of the perched water simulants used in these studies. These are as follows: (1) multiple physical/chemical forms, each having distinctly different mobilities,

are possible, (2) for time scales on the order of weeks and longer, the behavior of americium, thorium, and plutonium is dominated by solid forms, and (3) high mobility forms, the physical/chemical natures of which differ among the actinides, are possible. These findings have important implications regarding the behavior of actinide contaminants below the SDA and the conceptual models used to predict their transport.

Multiple physical/chemical forms, each having distinctly different mobilities, are possible: This phenomenon, which was not observed for strontium or uranium, was most pronounced for americium, thorium, and plutonium(IV) in the presence of EDTA and for neptunium in the presence and absence of EDTA. In these tests, the mobilities were characterized by a small (<1%) high mobility component with R<3, a large (≈50%) intermediate mobility component with 3<R<1000, and a large (≈50%) low mobility component with R>1000. This finding has significant implications with respect to modeling because it suggests that the traditional approach of using batch distribution coefficients (K_D) to infer contaminant mobility may not be appropriate for some contaminants in some situations. The key, of course, is identifying those situations where an alternate approach is warranted. For example, the plutonium(IV) – EDTA complex which was responsible for the intermediate mobility component in the experiments is a transient species which would only be important at the SDA in an episodic infiltration event such as a flood.

The behavior of americium, thorium, and plutonium is dominated by solid species of low mobility: In the absence of EDTA, more than 99% of the americium, thorium, and plutonium(IV) had low mobilities (R>1000) in the columns. This behavior is consistent with the thermodynamic phase diagrams which predict americium to be an insoluble carbonate or hydroxy-carbonate precipitate and thorium and plutonium(IV) to either be a hydroxide or an oxy-hydroxide polymer. The behavior is also consistent with sorption to silicate precipitates as speciation modeling predicts that the groundwater simulants are oversaturated with respect to silicates. Although not obvious, the behaviors of neptunium and plutonium(V) are also likely to be dominated by solid species. The neptunium data for "oxidized" columns and for normal columns at different flow rates both suggest reduction of neptunium(V) to neptunium(IV) by the interbed. Neptunium(IV) is hydrolyzed at pH 8 and likely forms the same immobile solid species as thorium and plutonium(IV). Plutonium(V) is more easily reduced than neptunium(V), and its low mobility component was greater than 99%, both in the presence and absence of EDTA. Thus, its behavior is likely governed by its reduction to the immobile plutonium(IV). The low mo-

bility of plutonium(V) is contingent on its encountering redox active constituents in the path of migration. This seems likely below the SDA.

In the laboratory columns uranium had high mobility (R≈3) due to the soluble complexes that it forms with carbonate. While the carbonate species are likely to control transport in the short term and would be important in episodic transport scenarios, long term transport is affected by aging processes and is likely dominated by insoluble calcium and/or phosphate mineral species. Since the solubilities of these uranium mineral species are typically much lower than the uranyl carbonates, long-term uranium mobility below the SDA is likely to be much lower than suggested by the column experiments.

High mobility forms are possible: High mobility forms were observed for americium, thorium, plutonium(IV), neptunium, and plutonium(V). The physical/chemical nature of these forms differed. Effluent filtrations showed the americium and neptunium high mobility form to be smaller than 3 nm, thorium to be larger than 3 nm, and plutonium(IV) and plutonium(V) to have portions both smaller and larger than 3 nm. When combined with batch filtration data and speciation modeling predictions, hypotheses are advanced regarding the nature of these high mobility forms as follows: americium – americium carbonate or hydroxy carbonate in either a soluble or small (<3 nm) precipitate form; thorium – thorium oxy-hydroxide polymer or hydrolyzed thorium sorbed to silicate precipitates (>3 nm); plutonium(IV) - plutonium oxy-hydroxide polymer or hydrolyzed plutonium sorbed to silicate precipitates; neptunium – soluble neptunium carbonate; plutonium(V) – plutonium carbonate complexes and the same species as above for plutonium(IV), due to reduction of plutonium(V) to plutonium(IV).

Collectively, these results provide a plausible explanation for the apparent disconnect between the transport model, which predicts interbed to be an effective barrier for plutonium and americium migration, and field data, which indicate penetration of that barrier. They are consistent with the transport model in that the column tests also show interbed to be an effective geochemical barrier (R>1000). They differ from the transport model however, in that the interbed was experimentally found to be effective for most of the americium and plutonium rather than all of it as predicted. The results are, at the same time, consistent with the field data. The high mobility forms appear to be at least partly colloidal, and the transport of colloidal material through the subsurface is likely to be stochastic. In fact, some of the breakthrough curves, particularly those for plutonium(V), not only had a high mobility component early in the test but also exhibited spo-

radic release of very small amounts throughout the duration of the experiment. This is consistent with the sporadic occurrence of americium and plutonium in monitoring data.

Additional findings of potential interest are the effect of mean linear velocity and the ability of the interbed matrix to attenuate colloids. Decreasing the mean linear velocity an order of magnitude below the value used in most of the tests did not affect retardation factors for any of the contaminants that were tested (neptunium, uranium, and strontium). These results provide a measure of assurance that behavior predicted by the columns may be applicable at the much lower mean linear velocities that are typical below the SDA. However, this extrapolation needs to be applied with care because there can be kinetic effects which are significant. For example, fractional recovery for neptunium declined when the flow rate was reduced because the increase in residence time provided for a greater reduction from neptunium(V) to neptunium(IV) by the soil. Similarly, the intermediate mobility fractions that resulted from EDTA complexation with americium, thorium, and plutonium(IV) were short lived. The ability of the 106 to 250 μm size fraction to attenuate colloids smaller than 20 nm was surprising and supports the findings that there is very little penetration of interbed by the colloidal forms.

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